

## MAGNITUDES AND SOURCES OF PRECIPITATION AND DRY DEPOSITION FLUXES OF INDUSTRIAL AND NATURAL LEADS TO THE NORTH PACIFIC AT ENEWETAK

Dorothy M. Settle and Clair C. Patterson

Division of Geological and Planetary Sciences, California  
Institute of Technology, Pasadena, California 91125

**Abstract.** A total atmospheric Pb input flux of  $7 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  was measured in the North Pacific Easterlies at Enewetak. Parameters used to measure this flux were ratio of dry deposition flux to precipitation flux;  $\text{Pb}/^{210}\text{Pb}$  in precipitation and seawater;  $^{210}\text{Pb}$  flux; washout factor; and Pb concentrations in air, rain, and dry deposition deposits. Relations among these parameters established at Enewetak were used to recompute and confirm previous estimates of lead fluxes to the oceans ( $\text{ng Pb cm}^{-2} \text{ yr}^{-1}$ ) at the following locations: North Atlantic Westerlies, 170; North Pacific Westerlies, 50; and South Pacific Easterlies, 3. Prehistoric lead output fluxes to sediments ( $\text{ng Pb cm}^{-2} \text{ yr}^{-1}$ ) at these locations have been previously measured and were 4 (Enewetak); 30 North Atlantic Westerlies; 3 North Pacific Westerlies; 4 South Pacific Easterlies. These data show that the rates of atmospheric inputs of lead to the oceans vary directly with variations in rates of upwind emissions of industrial lead from urban complexes on land. In the North Pacific and North Atlantic, present rates of atmospheric lead inputs are 10-fold greater than prehistoric outputs. In equatorial regions, present inputs and past outputs are more nearly equal. These observations disclose the effects of intense industrial atmospheric emissions of lead in the northern hemisphere westerlies which have overwhelmed prehistoric natural fluxes of lead to the oceans. The average concentration of lead in marine air at Enewetak is  $170 \text{ pg m}^{-3}$  and varies less than a factor of 2 from that mean. One to 15% of this lead comes from seaspray, while the remainder comes from sources on land. About 90% of the seaspray lead is industrial, while 80 to 99% of that originating from land sources is industrial. Concentrations of lead in rain at Enewetak range from 6 to 63  $\text{pg/g}$  with a mean value of 28. The mean precipitation flux, corrected for recycled lead in sea salts, measured by four different methods, was  $6 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ , while the net dry deposition flux measured on horizontal plastic plates was  $0.6 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ . The total dry deposition flux measured was  $6 \text{ ng cm}^{-2} \text{ yr}^{-1}$ , but 90% of this lead came from recycled seaspray. Lead isotope tracers show that Japan is the major source of industrial lead at Enewetak during the dry season, while the United States is the major source during the wet season.

## Introduction

Measurements of eolian lead fluxes to the oceans are important because it has been dis-

covered that industrial lead emissions to the earth's atmosphere outweigh natural contributions and have, as a consequence, perturbed biogeochemical cycles of lead in the oceans. Chow and Patterson [1962] noted that about 40 times more lead was reported to be entering oceans today via rivers than they found was leaving the oceans during prehistoric times via rivers in the form of authigenic lead in ferromanganese lattices in pelagic sediments. Tatsumoto and Patterson [1963a, b] and Chow and Patterson [1966] measured concentration profiles of lead in open ocean waters and found high concentrations near the surface which decreased to relatively constant values in deep waters. They ascribed the effects to eolian inputs of lead from automotive exhausts. Murozumi et al. [1969] found that Pb/Si dust ratios increased about 300-fold in Greenland snows during the past 3000 years. This indicated that industrial lead pollution was world wide and its effects should be observed in the world's oceans. It was then discovered [Patterson, 1974] that the early results of Tatsumoto and Patterson [1963a, b] and Chow and Patterson [1966] were erroneously high because contamination originating from the aura of artifact lead surrounding the ship and hydrowire befouled the sampling apparatus. Schaule and Patterson [1981, 1982] determined new concentration profiles of lead in North Atlantic and North Pacific waters and reported much lower concentrations of lead which still showed surface maxima and deep water minima. They correlated their data with  $^{210}\text{Pb}$  findings by Bacon et al., Bruland et al., Craig et al., and Turekian et al. [summaries in Schaule and Patterson [1981, 1982]] to show that lead has a residence time of several years in surface waters, about 20 years in the thermocline and about 80 years in deep waters. They ascribed maximal lead concentrations in upper waters to recent excess eolian inputs of industrial lead and correlated their observed greater lead contamination effects in North Atlantic surface waters compared with lesser contamination effects in North Pacific surface waters with corresponding differences in eolian input fluxes of industrial lead, computed by normalization to  $^{210}\text{Pb}$  input fluxes. Schaule and Patterson proposed that a switchover may have occurred from principally fluvial inputs of lead to the oceans in earlier times to principally eolian inputs of lead in recent times and that lead contamination effects in oceans of the southern hemisphere would not be as great as in the northern hemisphere because most industrial lead emissions occurred in the northern hemisphere. Presley had discovered that early lead concentration measurements reported in river waters were erroneously high [Trefry and Presley, 1976]. However, tentative present-day eolian input fluxes of lead to the open oceans suggested by

Copyright 1982 by the American Geophysical Union

Paper number 2C0858  
0148-0227/82/002C-0858\$05.00

Schaule and Patterson [1981, 1982] were nevertheless still about an order of magnitude larger than prehistoric output fluxes of authigenic lead in pelagic sediments in the same regions measured by Chow and Patterson [1962]. The input source of the latter was presumably fluvial at that time.

This study of eolian lead fluxes to the ocean in the North Pacific Easterlies was undertaken as part of the SEAREX Program [Duce, 1981] to distinguish quantitatively the relative and absolute contributions of lead via precipitation, dry deposition, and recycled seaspray. Additional aims of this study were to distinguish between natural and industrial leads in these fluxes by means of chemical ratios and common lead isotopic tracers and to determine their relative proportions. Relationships between common lead and  $^{210}\text{Pb}$  in the various components of these fluxes were also studied in collaboration with K. K. Turekian and J. K. Cochran. Results of this latter study have already been published [Settle et al., 1982]. Our findings reported here have a general applicability and have been used to recompute, from available data, eolian lead fluxes to the oceans in other geographic regions.

#### Sampling, Analyses, and Results

**Sampling.** The collection site was located at Enewetak ( $11^{\circ}20'\text{N}$ ,  $162^{\circ}20'\text{E}$ ). Air filter, rain, and dry deposition samples were collected atop a 20 m tower located on a small island on the upwind (east) side of the atoll during both the dry and wet seasons. An automatic system monitored wind direction and speed, condensation nuclei, temperature, humidity, and rainfall.

Millipore filters (47 mm, 0.4  $\mu\text{m}$  porosity) were mounted in plastic holders fitted with Kel F backstop frits and Teflon 'O' rings and suspended inside cylindrical conventional polyethylene rain shields (near the upper end) with 35 cm openings pointed down. Air was pumped at the rate of 15 lpm when meteorological conditions permitted easterly air masses uncontaminated by lead emissions from local sources to be sampled. The filters and holders were cleaned, assembled, and hermetically sealed in the ultra-clean laboratory at Caltech. After the samples were collected, the entire assembly was resealed and returned to Caltech. Later in the discussion section, data are cited that indicate that most of the atmospheric lead is contained in submicron particles and is not for the most part attached to giant seasalt particles. It has been suggested that our air filter configuration might discriminate against large seasalt particles and thereby miss a significant fraction of marine air lead. We had previously compared the relative collection efficiencies for lead in marine air of two different types of filter housings: an isokinetic arrangement, where the filter face was exposed normal to the wind direction of the marine air, and the type of inverted rain shield used at Enewetak. The experiments carried out at Pigeon Key, Florida [Patterson, 1981], showed no measurable bias in measured lead concentrations in marine air. Rain sampling procedures have been described in Settle et al. [1982]. The dry deposition collector was a circular polyethylene

plate about 3000  $\text{cm}^2$  upper surface area mounted horizontally in the prevailing air stream. After an exposure of 30 to 80 hours, the plate was placed in a clean air bench, and the dry deposition deposit was removed with 4 N  $\text{HNO}_3$ . About 8 ml of acid was ejected from a plastic squirt bottle along the outer rim of one quarter of the area of the plate. This liquid was then swept back and forth across the entire surface of the one-quarter segment by using a 4 mm diameter quartz rod 4 cm long attached at right angles to a quartz rod used as a handle. The liquid was worked to the center of the plate. The surface was slightly conical with a 1 cm diameter drain in the center. This operation was repeated for the remaining three quarters of the surface area of the plate, and then the entire operation was repeated twice more. All three washings were combined to provide a single dry deposition deposit sample. Next, the acid stripping procedure was repeated to collect an acid stripping blank. This liquid was set aside for blank analysis, and it was compared with a similar blank collected before the plate was exposed on the tower. A bottle container blank was obtained by placing some of the stripping acid in a fresh sample bottle and shipping it back with the samples. The lead content of the stripping acid was determined in previous separate experiments in the laboratory. Lead contamination added by the stripping acid bottle to the acid had also been previously determined in the laboratory. The deposit and blank solutions were returned to the laboratory in hermetically sealed conventional polyethylene bottles. Surface seawater was collected by hand dipping from the bow of a small boat as described in Schaule and Patterson [1981].

**Analyses.** Metals were analyzed by isotope dilution thermal emission mass spectrometry [Patterson and Settle, 1976]. Filters were cleaned by soaking in separate HCl and HF solutions. The filters were rinsed by soaking in small amounts of ultra-pure water and not by sucking water through the filter. A filter contributed 0.7 ng Pb and 0.5 ng Ba to the sample. Enriched  $^{208}\text{Pb}$  spike was added to the filter in a quartz dish, and it was dissolved by using a mixture of concentrated  $\text{HNO}_3$  and  $\text{HClO}_4$  in a filtered  $\text{N}_2$  atmosphere and evaporated to dryness. Lead was isolated by dithizone extraction for analysis in the mass spectrometer. Aliquots of the dissolved solution were spiked for alkalies and alkaline earths and were evaporated to dryness for analysis in the mass spectrometer with no further separation. Isotopic compositions of lead were determined in duplicate filters by using the procedures described above except that no lead spike was added. The reagent and ware lead blank for dissolving the filter, and isolating the lead was about 0.6 ng. The corresponding blank for barium was 0.1 ng.

The cleaning of bottles for rain collection are described in Patterson and Settle [1976]. The cleaning, use, and determination of blanks for the rain collector are described in Settle et al. [1982]. Total lead blank coming from the rain collector was about 4 ng/rain sample. An aliquot of rain, spiked with enriched  $^{208}\text{Pb}$ , was evaporated to dryness in quartz in the presence of a mixture of HCl and  $\text{HNO}_3$ . Metals were prepared for mass spectrometric analysis as

was indicated above. Chemical treatment blanks for these samples were 0.7 ng for Pb and 0.2 ng for Ba.

The dry deposition collector was cleaned in a manner similar to that for the rain collector, except that in the field the plate was treated with 4 N HNO<sub>3</sub> prior to exposure. The deposition collector lead blank for acid stripped dry deposition deposits was about 6 ng per sample. The samples were analyzed in the same manner as the rain samples described above. Chemical treatment blanks for these samples were 0.4 ng for Pb and 0.05 ng for Ba.

The analysis of seawater was done according to methods described by Schaule and Patterson [1981].

**Results.** Concentrations of metals in air, rain, seawater, and fluxes from dry deposition deposits are listed in Table 1. Uncertainties in metal concentrations in air amount to about 20% of reported values and originate mainly from large errors in determination of air sample volumes. In other samples, uncertainties are about 10% for lead and barium due mainly to lack of contamination control. Uncertainties for K, Ca, and Sr concentrations are about 1% for these samples. In most cases, corrections for lead contamination introduced during sampling and analysis were small fractions of the total amounts of lead measured. Lead isotopic compositions are reported in Table 2. Errors in the <sup>206</sup>Pb/<sup>207</sup>Pb are about 1 part in 1000, in the <sup>206</sup>Pb/<sup>208</sup>Pb about 2 parts in 1000, and in the <sup>206</sup>Pb/<sup>204</sup>Pb about 4 parts in 1000.

Dust concentrations were calculated from barium concentrations multiplied by 2500, which corresponds to the average abundance of barium in crustal silicate rocks [Mason, 1960]. The ratios of barium to silicate dusts in the samples we studied probably did not differ more than two-fold from this factor. Parallel air filter samples were collected by the URI and CIT groups. Our reported silicate concentrations, determined on the basis of barium, agree closely with their reported silicate concentrations, determined on the basis of aluminum. Virtually all the barium in the samples listed in Table 1 can be ascribed to silicate dust. The other major mass constituent in these samples is seasalt, which contains extremely low concentrations of barium on a mass basis relative to silicate dust. Measurements were made of the Ba/Ca ratios in these samples, and in all cases they were found to be far greater than the Ba/Ca ratio in seasalt. This verified the above use of barium as an indicator of silicate. Measurements of concentrations of potassium and strontium were also made so that resulting K/Ca and Sr/Ca ratios could be used to verify the supposition that nearly all of the calcium was of seasalt origin. Rb/K ratios were determined to check the internal consistencies of these measurements.

The Rb/K ratios in air during the dry season were found to be anomalously high. However, the Sr/Ca ratios also showed crustal silicate values. The air contained excessive concentrations of silicate dust during this season (see discussion section). Rb/K ratios exceed average crustal values, and this may characterize the Asian region from which these dusts apparently originated (see later discussion).

The Ca/Sr ratio in rain and dry deposition is

54.8 ( $\sigma = 2.5$ ). The average Ca/Sr ratio in seawater is 52.2 [Pytkowicz and Kester, 1971], which, when corrected for the biogenic depletion of calcium relative to strontium in surface seawater [Broecker, 1974], reduces to about 51.6. The difference between this latter value and our mean observed value exceeds our experimental measurement error. This difference cannot be ascribed to silicate dust (Ca/Sr  $\approx$  80) perturbation because the effect is larger than that which could be produced by dust and the variations observed are inversely correlated with dust concentrations, as determined by Sr/Ba ratios (Sr/Ba in seawater  $\sim$  400; in silicate dust  $\sim$  2). Either the principle upon which the biogenic depletion of calcium relative to strontium is based is in error, or there is some unknown mechanism that enhances calcium relative to strontium in seaspray salt.

#### Magnitudes of Fluxes

**Precipitation fluxes.** Lead precipitation fluxes to the ocean were determined by four methods: (1) measured [ng Pb/kg rain]  $\times$  mean [kg rain cm<sup>-2</sup> yr<sup>-1</sup>] = ng Pb cm<sup>-2</sup> yr<sup>-1</sup>; (2) mean [ng Pb/dpm <sup>210</sup>Pb in rain]  $\times$  [dpm <sup>210</sup>Pb cm<sup>-2</sup> yr<sup>-1</sup> total to sea] = ng Pb cm<sup>-2</sup> yr<sup>-1</sup>; (3) [ng Pb/dpm <sup>210</sup>Pb in surface seawater]  $\times$  [dpm <sup>210</sup>Pb cm<sup>-2</sup> yr<sup>-1</sup> total to sea] = ng Pb cm<sup>-2</sup> yr<sup>-1</sup>; and (4) washout factor (derived from measurements made during a different time or season of ([ng Pb/kg rain] + [ng Pb/m<sup>3</sup> air])  $\times$  [ng Pb/m<sup>3</sup> air] (for the required time or season)  $\times$  [kg rain cm<sup>-2</sup> yr<sup>-1</sup>] = ng Pb/cm<sup>-2</sup> yr<sup>-1</sup>. Rains were collected during two different climatic regimes, the dry season and the wet season. One rain sample was collected during the dry season and eight during the wet. Five of the nine samples collected were analyzed for six metals whose concentrations are given in Table 1. The volume of one of the remaining samples was too small to analyze for lead, while the volumes of two others were too small to analyze for both lead and <sup>210</sup>Pb. One sample was not analyzed because of known probable contamination from local lead emissions. The lead concentration in the May 16 rain sample (the only one collected during the dry season) was discarded after analysis because it was concluded that it probably had been contaminated by an overflight through the rain cloud of an aircraft that was observed to land after the rain sample had been collected. Because no scientifically useful rain samples for lead concentrations were collected during the dry season, it was necessary to invoke method 4 to compute a precipitation flux for the dry season.

Lead precipitation fluxes determined from the samples listed in Table 1 by methods 1, 2, and 3 above have been discussed by Settle et al. [1982], and are revised as follows.

Method 1. A mean concentration of 28 pg Pb/g rain from 3 samples collected during the wet season (July 19 omitted, see following discussion), assumed to represent the mean yearly concentration, was used with a mean annual precipitation of 130 cm yr<sup>-1</sup> near Enewetak [Dorman and Bourke, 1979] to calculate a lead precipitation flux of 4 ng Pb/cm<sup>-2</sup> yr<sup>-1</sup>.

Method 2. A ratio of 65 ng Pb/dpm <sup>210</sup>Pb in rain [Settle et al., 1982] was used with a total <sup>210</sup>Pb flux of 0.15 dpm cm<sup>-2</sup> yr<sup>-1</sup> to the sea near

TABLE 1. Concentrations of Metals, Silicate Dust, and Seasalt in Rain and Air, and Dry Deposition Fluxes at Enewetak.

Sample Type	Collection Dates 1979	Sample Size	Pb	K	Rb	Ca	Sr	Ba	Si dust*	Seasalt**
Rain (ng/kg)	May 16	1 kg	(54)***	43000	16	-	-	35	87000	3.7 x 10 <sup>6</sup>
	July 19	2 kg	6	98000	32	100000	1900	94	230000	8.3 x 10 <sup>6</sup>
	July 27	2 kg	17	27000		28000	520	< 0.6	< 1500	2.4 x 10 <sup>6</sup>
	Aug. 2	1 kg	63	46000	14	47000	860	8.6	22000	4.0 x 10 <sup>6</sup>
	Aug. 3	2 kg	6	19000	7	16000	290	0.25	630	1.6 x 10 <sup>6</sup>
	Oct. 3 (1980)\$	1 kg	43	43000	13	44000	800	120	290000	3.1 x 10 <sup>6</sup>
Dry Deposition (ng/cm <sup>2</sup> yr)	April 24-27†	30 hr	12	24000	-	29000	500	8.5	21000	2.2 x 10 <sup>6</sup>
	April 28-29†	28 hr	6	34000	-	39000	690	3.1	7700	3.2 x 10 <sup>6</sup>
	July 14-Aug. 11†	80 hr	4	15000	4	15000	300	1.8	4600	1.2 x 10 <sup>6</sup>
	April 22-28††	7 days	2	320	0.15	500	9	0.94	2300	2.9 x 10 <sup>4</sup>
	April 28-May 9††	12 days	7	1400	0.84	1400	26	2.4	6000	10.5 x 10 <sup>4</sup>
	July 25-Aug. 10††	22 days	0.1	780	0.22	710	13	1.3	3300	5.7 x 10 <sup>4</sup>
Air (ng/m <sup>3</sup> )	April 22-28	87 m <sup>3</sup>	0.26	330	5.7	320	4	0.66	1600	2.4 x 10 <sup>4</sup>
	April 28-May 9	143 m <sup>3</sup>	0.21	260	5.3	260	4	1.4	3400	1.4 x 10 <sup>4</sup>
	July 12-25	142 m <sup>3</sup>	0.088	120	0.09	140	2.5	0.025	63	1.1 x 10 <sup>4</sup>
	July 25-Aug. 10	141 m <sup>3</sup>	0.15	120	0.03	130	2	0.011	28	1.1 x 10 <sup>4</sup>
Surface seawater (ng/kg)	Aug 14	2 kg	6.5							

\* Si dust from Ba.  
\*\* Seasalt from K and Ca concentration after correcting for dust.  
\*\*\* Observed lead value (110) rejected because aircraft flew through rain cloud, but dust and salt values retained.  
Listed Pb concentration computed from washout factor and air concentration (see text).  
\$ Collected 40°E of Enewetak aboard R.V. Thompson.  
† Plate deposition surface facing upward.  
†† Filter deposition surface facing downward.

TABLE 2. Isotopic Compositions of Lead in Rain, Dry Deposition, and Air and in Surface Seawater at Enewetak.

Sample Type	Collection Dates, 1979	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}/^{208}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$
Rain	May 16	1.212†	0.4940†	19.32†
Rain	July 27	1.241	0.5060	19.36
Rain	Oct. 3 (1980)*	1.206	0.4925	19.03
Dry deposition	April 24-27	1.221	0.4965	19.03
Dry deposition	April 28-29	1.225	0.4993	19.21
Dry deposition	July 14-Aug. 11	1.227	0.4979	19.16
Air	April 22-May 9	1.170	0.4858	18.26
Air	May 9-15	1.196	0.4889	18.61
Air	July 22-Aug. 10	1.205	0.4908	18.84
Surface seawater	Aug. 14	1.184	0.4861	18.38

  

Surface Seawater 150° to 160° W longitude collected in 1979**				
Latitude	Concentration (ng/kg)	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}/^{208}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$
15°N	10.7	1.196	0.4892	19.20
4°N	6.5	1.182	0.4843	18.24
2°S	5.1	1.176	0.4836	18.06
8°S	4.6	1.174	0.4856	-
15°S	4.2	1.176	0.4813	18.68

† Values rejected (see text).

\* Collected 40° E of Enewetak aboard R. V. Thompson.

\*\* From Flegal et al. [1981].

Enewetak [Turekian and Cochran, 1981] to calculate a lead precipitation flux of  $10 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ . The total  $^{210}\text{Pb}$  flux used in method 2 was determined with a funnel left continuously exposed so that it collected both dry deposition and precipitation. Turekian and Cochran [Settle et al., 1982] observed that the dry deposition component of  $^{210}\text{Pb}$  was negligible. The total  $^{210}\text{Pb}$  flux is used as a pure precipitation flux for common lead for this reason. The speciation of  $^{210}\text{Pb}$  in marine aerosols is apparently different than that of lead which accounts for the difference in dry deposition fluxes and their different ratios in air and in precipitation.

Method 3. A  $\text{Pb/dpm } ^{210}\text{Pb}$  ratio of  $37 \text{ ng Pb/dpm } ^{210}\text{Pb}$  in surface seawater near Enewetak (lead concentration from this study,  $\text{dpm } ^{210}\text{Pb}$  concentration from Nozaki et al. [1976], and Nozaki et al. [1980]) was used with a  $^{210}\text{Pb}$  precipitation flux of  $0.15 \text{ dpm cm}^{-2} \text{ yr}^{-1}$  to calculate a lead precipitation flux of  $6 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ . It is possible that the precipitation mechanisms for lead and  $^{210}\text{Pb}$  involved in method 3 are not the same. The  $\text{ng Pb/dpm } ^{210}\text{Pb}$  ratio in air during the wet season was about 20, which is considerably less than the ratio of 65 observed in rain collected during this same period ( $^{210}\text{Pb}$

in air from Turekian and Cochran [1981]). In calculating a precipitation flux by using the ratio of  $\text{ng Pb/dpm } ^{210}\text{Pb}$  in surface seawater, no correction was made for  $^{210}\text{Pb}$  produced by  $^{226}\text{Ra}$  in that water. It is believed that this correction should be small (K.K. Turekian, personal communication, 1981) because the amount of  $^{210}\text{Pb}$  emitted into the atmosphere from the continents on a global scale is 2 orders of magnitude greater than the amount of  $^{210}\text{Pb}$  produced by  $^{226}\text{Ra}$  in the upper 100 m of the world's oceans [Nozaki et al., 1976; Nozaki et al., 1978; Nozaki et al., 1980], and a major fraction of the continent-derived  $^{210}\text{Pb}$  is introduced to the ocean surfaces.

$^{210}\text{Pb}$  flux methods are meritorious and highly useful, nevertheless, because it appears difficult to avoid spurious contamination of rain from emissions of locally derived Pb by updrafts into air masses producing the rain [Settle et al., 1982].

Method 4. A precipitation flux for the dry season can be computed from a mean concentration of  $230 \text{ pg Pb/m}^3$  air during that period and a washout factor of 230 (determined from  $28 \text{ ng Pb/kg rain}$  and  $0.12 \text{ ng Pb/m}^3$  air measured during the wet season). The concentration of  $54 \text{ pg Pb/g}$

rain during the dry season computed in this way seems to be a good approximation because the Pb/dpm  $^{210}\text{Pb}$  ratio computed from it for dry season rain is 100 which is comparable to the mean of 70 measured in wet season rains. A lead precipitation flux of  $7 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  was calculated in this way for the dry season.

Washout factor theory predicts that the ratio (Pb in precipitation)/(Pb in air) is constant for different locations regardless of changes in absolute concentrations [Engelmann, 1970]. Original lead data that seemed to validate this theory were actually erroneously high due to contamination during collection and analysis. Reliable data for lead in precipitation and air show that the washout factor cannot be used for urban or suburban locations. The observed washout factor is anomalously low in such places because the precipitation is not formed in the highly polluted air near the ground (which is the source of the air samples). The washout factor for lead is observed to vary from 640 ( $\text{ng Pb kg}^{-1}/\text{ng Pb m}^{-3}$ ) in Greenland snow [Davidson et al., 1981] to 330 in remote California High Sierra snow [Elias et al., 1982] to 230 in North Pacific Easterlies (this paper) to 220 in the North Atlantic Westerlies rain [Bruland et al., 1982] to 270 in South Pacific Easterlies rain (D.M. Settle and C.C. Patterson, unpublished manuscript, 1982) to 150 in Caribbean Easterlies rain perturbed by coastal urban air [Patterson and Settle, 1979; Settle et al., 1982], with about a 1000-fold range of lead concentrations in precipitation and in air, yielding a mean value of 300 for the washout factor.

The agreement among Pb precipitation fluxes derived from four methods, each having a unique defect not common to the other three, suggests that the probable value of the total Pb precipitation flux from both land sources and seaspray in the North Pacific Easterlies lies in the range of  $4\text{--}10 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ , with a mean of  $7 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ . On the basis of considerations discussed later in the section on dry deposition fluxes, it is estimated that the proportion of seawater lead in marine air recycled as seaspray can be determined by multiplying the concentration of NaCl in the air by a Pb/NaCl ratio of  $1 \times 10^{-6}$ . Assuming these same relationships hold for recycled seaspray lead in marine precipitation, it is observed that except for one rain (July 19), about 10% of the lead in marine rain appears to be recycled from seaspray (the July 19 rain appears to contain mostly recycled seaspray lead). The mean net precipitation flux of lead from land sources is then  $6 \text{ ng cm}^{-2} \text{ yr}^{-1}$ .

**Dry deposition fluxes.** Dry deposition fluxes were determined from deposits collected on the upper surface of a circular horizontal conventional polyethylene plate. The plate was supported from the bottom and had no rim. Dry deposition fluxes for seasalts and silicate dusts as well as lead were determined on this device. Dry deposition deposits on horizontal millipore filter surfaces, exposed downward from the top center within a vertically mounted large cylindrical polyethylene rain shield whose height to diameter aspect ratio was 1:1, were analyzed to make corrections for exposure blanks on other filters used to sample filtered air. These data were also used to compute dry deposition fluxes

on a horizontal surface exposed downward.

Total dry deposition fluxes of 9 and  $4 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  (which includes both recycled seaspray lead and atmospheric lead derived from land sources) were obtained during the dry and wet season respectively on the plate oriented upward. Total dry deposition fluxes of 7 and  $2 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  were obtained during the dry season and of  $0.1 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  during the wet season on millipore filters oriented downward within a rain shield. As will be discussed below, 90% of the lead measured on the plates comes from recycled seaspray, so net dry deposition fluxes of  $0.9$  and  $0.4 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  were measured on the upward facing plates during the dry and wet season, and net fluxes of  $0.7$ ,  $0.2$ , and  $0.02 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  were obtained on the downward facing millipore filters. Downward deposition fluxes on the plate facing upward involve high transfer velocities and large particles. In two instances (Table 1) the upward deposition fluxes on the sheltered filters facing downward were considerably less than the downward fluxes on the openly exposed plates for the same collection period. This suggests that a smaller fraction of large particles were being collected in the upward direction on the filters. However, in one instance (Table 1) the upward deposition flux on a filter was equal to the downward flux on the exposed plate. The deposition flux of  $7 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  in this last case occurred when the mean wind velocity was  $10 \text{ m s}^{-1}$ , while the deposition flux on the filters dropped precipitously to  $2 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  with a decrease in wind velocity to  $9 \text{ m s}^{-1}$ , and to  $0.1 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  when the mean wind velocity decreased to  $7 \text{ m s}^{-1}$ . It is significant that the upward deposition velocities on these downward facing surfaces varied by a factor of 40, while mean wind speeds varied by only about 30%. The complex aerodynamic properties of the downward facing millipore filter deposition collector makes it unsuitable as a deposition monitoring device for ocean surfaces. On the other hand, it is not possible to translate deposition fluxes on the openly exposed upward facing plastic plate directly to ocean surfaces. The fluxes of fine particle components are dependent upon gas velocities across the horizontal surfaces so there is no way to translate through model calculations the undulating surface of the ocean to a monitor consisting of a fixed, rigid, horizontal surface. In approximate terms, however, the horizontal plate measurements yield useful dry deposition flux information because most of the deposited lead seems to be attached to large seasalt particles [Settle et al., 1981]. This conclusion is based on considerations outlined below. It was estimated from visual observations that the surface of the conventional polyethylene plate was soon thickly covered with a deposit of  $>100 \mu\text{m}$  sized salty droplets, rendered hygroscopic, and attached to the plate because of its acid conditioning, so we believe that there was little subsequent loss of micron-sized particles by reentrainment. At present, our best estimate of the total dry deposition flux of lead from both land and recycled seaspray to the ocean surface in the North Pacific Easterlies is about  $6 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ .

It is important to know what are the propor-

tions of the above dry deposition flux of lead originating from seawater lead recycled as spray and coming from lead-rich aerosols generated over continental regions. The average isotopic composition of dry deposition lead ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.226$ , Table 2) compared with the average isotopic composition of atmospheric lead ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.190$ , Table 2) proves that dry deposition lead must be derived from only a fraction of the total lead in air. We believe that most of the dry deposition lead is attached to large seasalt particles, first because mass inventory considerations suggest that much of this kind of lead probably originates from seaspray, and second, isotopic relationships among leads in precipitation, dry deposition, air, and seawater guide us to this conclusion.

On the basis of a suggestion by Fasching et al. [1974], we and our colleagues carried out experiments in the North Atlantic (part of the SEAREX program using a bubble generating device provided by Fasching) which sampled and analyzed lead and other metals in artificial sprays [Patterson and Ng, 1982]. These experiments suggest that Pb/NaCl ratios in seaspray aerosols are enriched by a factor of about 500-fold above the ratio in seawater. The ratio of Pb/NaCl in surface seawater measured at Enewetak (Table 1) can be multiplied by a 500-fold enrichment factor to yield a predicted value of about  $1 \times 10^{-7}$  for the Pb/NaCl ratio in air at Enewetak. Duce et al. [1982] have measured the size-frequency distribution of both NaCl and lead-containing particles at Enewetak and have found that about 90% of the NaCl exists in particles larger than  $4 \mu\text{m}$ , while only about 10% of the total lead in the atmosphere is contained in particles of that size (we have verified the accuracy of their total lead concentration measurements). If these proportions are combined with the total concentrations of lead and seasalts in air listed in Table 1, a Pb/NaCl ratio of about  $10 \times 10^{-7}$  is found in air for both the wet and dry season. The Pb/NaCl ratio measured directly in dry deposition is about  $30 \times 10^{-7}$  for both the wet and dry season. Since the 500-fold lead enrichment factor in seaspray is known only approximately at present, we believe that this first-order agreement of mass inventory considerations for lead in seaspray salt shows that the lead in marine dry deposition deposits is mainly recycled seawater lead.

The isotopic relationship among leads that guide us to this same conclusion show that rain today at Enewetak contains lead whose average isotopic composition ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.227$ , Table 2) is markedly different from that in seawater ( $^{206}\text{Pb}/^{207}\text{Pb} = 1.184$ , Table 2). Some of the lead in rain is contained in discrete particles that become trapped in the organic microlayer on the sea surface and have a residence time there of hours and perhaps days before the lead is released in soluble form to become homogenized with the reservoir of dissolved lead in surface seawater. Schaule and Patterson [1981, 1982] have observed that about 10% of the lead in open ocean seawater is contained in particles, while Buat-Menard et al. [1981] have shown that seaspray contains relatively large hydrocarbon particles in which are embedded smaller silicate dust particles. We believe that much of the lead

contained in seaspray aerosols originates from lead-rich particles trapped in the surface microlayer. At any given time, the isotopic composition of lead in seaspray should be similar to that in precipitation. This is observed to be the case if lead in dry deposition originates from seaspray,  $^{206}\text{Pb}/^{207}\text{Pb} = 1.226$  in dry deposition, and 1.227 in rain during the wet season at Enewetak.

The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio in atmospheric leads originating from North American regions is about 1.235 (Table 2), and during the wet season the values of this ratio in rain indicate that most of the lead in precipitation comes from North American sources. About 90% of this land component type of lead is required to be mixed with about 10% of seawater lead near Enewetak to account for the observed isotopic mixture in the dry deposition deposits (Table 2). This suggests that the major amount of lead in seaspray is recycled from recently deposited lead in precipitation.

The major fraction of lead in marine dry deposition should therefore be assigned to recycled lead from the surface microlayer. Because of uncertainties in the above considerations, we assign 90% of the dry deposition flux to recycled microlayer seawater lead and 10% to continental sources.

Relative magnitudes and sum of precipitation and dry deposition fluxes. We and our colleagues have made careful measurements of the proportion of precipitation to dry deposition fluxes of lead at a remote mountain location in Western North America [Elias et al., 1982];  $270 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  were added to the meadow and forested ecosystem by dry deposition, while  $130 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  were added to that ecosystem by snow and rain. Ninety-nine percent of the lead was industrial. Dry deposition is the predominant mechanism for removing lead from the atmosphere over land because plant foliage has such a large surface area for collecting by diffusion deposition the small anthropogenic particles which contain the industrial lead. The Enewetak experiments confirm our belief that, because the area of the ocean surface is relatively small, the net dry deposition lead flux to the ocean is minor. At Enewetak we observed a dry deposition flux of lead from continental sources of about 10% of the precipitation flux. The remainder of the lead measured on the dry deposition plates originates from recycled seaspray lead. Our best estimates of the net precipitation flux of lead from land sources to the ocean in the North Pacific Easterlies is about  $6 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ , while the net dry deposition flux from land sources is about  $0.6 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ , yielding a total net input flux of  $7 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ .

#### Relation of Fluxes at Enewetak to Other Ocean Areas

The measured  $7 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  atmospheric input flux to the ocean at Enewetak represents that in the region of North Pacific Easterlies. The flux does not increase at eastern longitudes, as measurements made at  $160^\circ\text{W}$  show (Table 3). Sophisticated measurements made at Enewetak allow sketchy measurements made at other oceanic locations to be converted into more

TABLE 3. Present Day Eolian Input and Prehistoric Sediment Output Lead Fluxes at Different Locations ( $\text{ng cm}^{-2} \text{ yr}^{-1}$ ).

	North Atlantic Westerlies (34°N 66°W)	North Pacific Westerlies (33°N 140°W)	North Pacific Easterlies (11°N 162°E)	North Pacific Easterlies (15°N 160°W)	South Pacific Easterlies (15°S 150°W)
Input	170	50	7	6	3
Output	30	3	4	4	4

Output fluxes computed using sediment parameters cited in Schaule and Patterson [1981] and lead concentration data from Chow and Patterson [1962].

trustworthy fluxes by making corrections for dry deposition and using a washout factor where atmospheric lead concentrations have been measured to give approximate concentrations of lead in rain at these locations. The present total atmospheric input flux to the ocean has been estimated to be about  $240 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  in the region of the North Atlantic Westerlies [Schaule and Patterson, 1982], about  $60 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  in the region of the North Pacific Westerlies [Schaule and Patterson, 1981], and about  $4 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  in the region of the South Pacific Easterlies [Settle et al., 1982].

The Enewetak measurements modify these estimates, mainly by reducing the dry deposition contribution as follows:

Mean Total Flux =  $170 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  in North Atlantic Westerlies Region

1.  $2.4 \text{ [ng Pb m}^{-3} \text{ air]}$  [Patterson and Ng, 1982]  $\times 0.9$  (corrected for recycled seaspray, this paper)  $\times 220 \text{ [kg rain}^{-1} \text{ m}^3 \text{ air]}$  (washout factor, Patterson and Ng [1982])  $\times 0.1 \text{ [kg rain cm}^{-2} \text{ yr}^{-1}]$  [Tucker, 1961]  $\times 1.1$  (dry deposition contribution, this paper) =  $55 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ .

2.  $190 \text{ [ng Pb kg}^{-1} \text{ sea/dpm } ^{210}\text{Pb kg}^{-1} \text{ sea}]$  [Bruland et al., 1982]  $\times 0.7 \text{ [dpm } ^{210}\text{Pb cm}^{-2} \text{ yr}^{-1} \text{ total to sea}]$  [Turekian et al., 1982] =  $130 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ .

3.  $37 \text{ [ng Pb kg}^{-1}]$  [Schaule and Patterson, 1982]  $\times 10 \text{ [kg cm}^{-2}]$  (depth of surface layer)  $\div 2 \text{ yr}$  (residence time, Schaule and Patterson [1982]) =  $190 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ .

4.  $390 \text{ [ng Pb kg}^{-1} \text{ rain/dpm } ^{210}\text{Pb kg}^{-1} \text{ rain}]$  [Bruland et al., 1982]  $\times 0.9$  (corrected for recycled seaspray, this paper)  $\times 0.7 \text{ [dpm } ^{210}\text{Pb cm}^{-2} \text{ yr}^{-1} \text{ total to sea}]$  [Turekian et al., 1982]  $\times 1.1$  (dry deposition contribution, this paper) =  $275 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ .

Mean Total Flux =  $50 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  in North Pacific Westerlies Region

1.  $1 \text{ [ng Pb m}^{-3} \text{ air]}$  [Chow et al., 1969]  $\times 0.9$  (corrected for recycled seaspray, this paper)  $\times 230 \text{ [kg rain}^{-1} \text{ m}^3 \text{ air]}$  (washout factor, this paper)  $\times 0.13 \text{ [kg rain cm}^{-2} \text{ yr}^{-1}]$  [Dorman and Bourke, 1979]  $\times 1.1$  (dry deposition contribution, this paper) =  $30 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ .

2.  $60 \text{ [ng Pb kg}^{-1} \text{ sea/dpm } ^{210}\text{Pb kg}^{-1} \text{ sea}]$  [Schaule and Patterson, 1982]  $\times 1 \text{ [dpm } ^{210}\text{Pb cm}^{-2} \text{ yr}^{-1} \text{ to sea}]$  [Nozaki et al., 1980] =  $60 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ .

3.  $10 \text{ [ng Pb kg}^{-1}]$  [Schaule and Patterson, 1981]  $\times 10 \text{ [kg cm}^{-2}]$  (depth of surface layer)  $\div 2 \text{ yr}$  (residence time, Schaule and Patterson [1981]) =  $50 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ .

4.  $65 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  (from mass balance of industrial lead emission and removal in northern hemisphere westerlies, Schaule [1979]).

Mean Total Flux =  $6 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  in North Pacific Easterlies Region:  $15^\circ\text{N}$ ,  $160^\circ\text{W}$  ( $40^\circ$  east of Enewetak)

1.  $43 \text{ [ng Pb kg}^{-1} \text{ rain}]$  (this paper)  $\times 0.9$  (corrected for recycled seaspray, this paper)  $\times 0.13 \text{ [kg rain cm}^{-2} \text{ yr}^{-1}]$  [Dorman and Bourke, 1979]  $\times 1.1$  (dry deposition contribution, this paper).

Mean Total Flux =  $3 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$  in South Pacific Easterlies Region

1.  $9 \text{ [ng Pb kg}^{-1} \text{ rain}]$  [Settle et al., 1982]  $\times 0.9$  (corrected for recycled seaspray, this paper)  $\times 0.15 \text{ [kg rain cm}^{-2} \text{ yr}^{-1}]$  [Dorman and Bourke, 1979]  $\times 1.1$  (dry deposition contribution, this paper) =  $1.3 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ .

2.  $14 \text{ [ng Pb kg}^{-1} \text{ rain/dpm } ^{210}\text{Pb kg}^{-1} \text{ rain}]$  [Settle et al., 1982]  $\times 0.9$  (corrected for recycled seaspray, this paper)  $\times 0.3 \text{ [dpm } ^{210}\text{Pb cm}^{-2} \text{ yr}^{-1} \text{ total to sea}]$  [Turekian et al., 1977]  $\times 1.1$  (dry deposition contribution, this paper) =  $3.9 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$ .

The measured net eolian input flux of lead to the ocean at Enewetak experimentally confirms the global pattern of fluxes expected from emissions of industrial lead into the northern hemisphere westerlies. Since the largest sources of these emissions, which outweigh natural ones by about 2 orders of magnitude, are in North America and in Europe and lead is rapidly removed by dry deposition and precipitation, the input flux of lead to the ocean should be highest in the North Atlantic Westerlies, less in the North Pacific Westerlies, lower in the North Pacific Easterlies, and still lower in the South Pacific



Easterlies. As shown in Table 3, the net fluxes are 170, 50, 7, 6, and 3 ng Pb cm<sup>-2</sup> yr<sup>-1</sup>, respectively, at these five locations.

These input fluxes are composed mainly of industrial lead. The present magnitudes of all are much greater than the magnitudes of natural eolian lead input fluxes to the oceans during prehistoric times. It is believed that the major source of lead to the oceans in prehistoric times was fluvial, and, because steady state conditions prevailed, fluvial input fluxes beyond the continental shelves were equal to the output fluxes measured in pelagic sediments (listed in Table 3). This view is substantiated not only by mass balance considerations [Schaule and Patterson, 1980] but required by isotopic relationships among leads in pelagic sediments and continental drainage basins [Chow and Patterson, 1962]. These relationships show that prehistoric eolian input fluxes of natural lead were small fractions of the sediment output fluxes listed in Table 3. Present day eolian input fluxes of industrial lead therefore exceed past eolian input fluxes by factors of about 3 to 50 depending on the geographic location.

The prehistoric net flux of soluble lead from surface waters down through the water column via fecal pellets then out through Pleistocene sediments in authigenic minerals in regions of both the North Pacific Easterlies and South Pacific Easterlies is about 4 ng Pb cm<sup>-2</sup> yr<sup>-1</sup> (Table 3). As shown in this table, the similarity of present input and prehistoric output fluxes of lead measured in the South Pacific Easterlies region presents a sharp contrast to the situation in the North Pacific and North Atlantic Westerlies regions, where present day eolian input fluxes are an order of magnitude larger than prehistoric output fluxes.

It has been observed that present-day vertical lead concentration profiles of seawater in the North Pacific and North Atlantic Westerlies regions are highly perturbed compared with inferred prehistoric natural concentration profiles as a consequence of this shift from relatively small lead input via natural fluvial routes to much greater industrial lead inputs via eolian routes during the past century and the 20 yr and 80 yr residence times of lead in thermocline and deep waters [Schaule and Patterson, 1982]. We expect, as a consequence, that present-day vertical lead concentration profiles in easterly North Pacific seawaters would show less perturbation than those in waters at more northerly latitudes, with lead concentrations in thermocline waters being shifted to lower values compared to those observed in the North Pacific Westerlies region.

#### Origins of Marine Lead

**Sources of marine lead.** Table 4 shows that the Pb/silicate ratio in air, dry deposition, and rain at Enewetak exceeds the average crustal rock value by large factors. A mass inventory of natural and industrial emissions to the atmosphere on a global scale shows that most of this excess originates from industrial sources. The prehistoric natural lead input to the world atmosphere from silicate dust was about 2000 tons Pb yr<sup>-1</sup> [Settle and Patterson, 1980]. Although

this value is not very certain, silicate dusts by definition cannot account for the observed excess, since the Pb/silicate ratio in the atmosphere, when reliably measured in remote regions, always shows a large excess above the average crustal silicate value (Table 4). The present-day flux of industrial lead to the world atmosphere is about 400,000 tons yr<sup>-1</sup> from burned lead alkyls; iron, copper, lead, and zinc smelting; coal burning; and wind-blown dusts from lead contaminated soils [Nriagu, 1978]. About half of this lead is emitted in the form of long-lived aerosols that are distributed world wide [Settle and Patterson, 1980]. The literature contains a number of reports of erroneous measurements of Pb/silicate ratios in air and polar snow that are falsely high because of improperly controlled lead contamination during sample collection and/or analyses. These large excesses of lead have been improperly ascribed to natural sources such as seaspray emission, vulcanism, sublimation from rocks at low temperatures, and emission of volatile organo-lead compounds from soils and plants. We have studied natural lead emissions from seaspray and volcanoes on a quantitative basis and have found, as reported above, that recycled lead in seaspray contributes about 10% of the lead in the North Pacific Easterlies. Since about 90% of that seaspray lead has been shown to be of industrial origin [Schaule and Patterson, 1981], it is clear that natural seawater lead could comprise only about 1% of lead in marine air. We and others [Buat-Menard and Arnold, 1978; Patterson et al., 1982; Arnold et al., 1981] have recently demonstrated from measurements of Pb/S ratios in volcano eruption plumes, normalized to worldwide volcanic sulfur fluxes to the atmosphere, that the average contribution of lead from volcanoes in the form of lead-rich sulfur aerosols to the world atmosphere is about 1500 tons Pb yr<sup>-1</sup>. On a world scale, excess lead originating from industrial sources should completely obscure excess lead from volcanoes and seaspray. The other proposed sources for excess natural lead cannot be quantitatively considered because of their vagueness. In the northern hemisphere it has been demonstrated conclusively that the Pb/silicate ratio in Greenland ice increased about 300-fold during the past 3000 years [Murozumi et al., 1969; Ng and Patterson, 1981]. This would not have happened if the excess lead originated from natural sources.

Industrial leads emitted from different countries have various isotopic compositions because the geological origins of the metal ores supplied to these nations are different. For example, lead emitted from Japan tends to be relatively nonradiogenic because most of the iron ores and lead used in that country originate from geologically ancient deposits in Australia, while lead emitted today from the United States is highly radiogenic because a major fraction of U.S. industrial lead originates from Missouri ore deposits whose isotopic compositions are anomalously radiogenic. The isotopic compositions of industrial leads emitted from other countries vary for similar reasons, and estimates of these isotopic compositions are listed in Table 5. The <sup>206</sup>Pb/<sup>207</sup>Pb ratio is the most accurately measured pair among the four lead isotopes, and it shows the greatest variation among different lead ores, so

TABLE 4. Excess Pb Over Natural Pb/Si Dust in Rain, Dry Deposition, and Air Collected at Enewetak and Other Remote Locations

Sample Type	Collection dates (1979)	Pb/Si dust	Excess over crustal
Enewetak			
Rain	May 16	$(5.3 \times 10^{-4})^\dagger$	$(44)^\dagger$
Rain	July 19	$2.2 \times 10^{-5}$	2
Rain	July 27	$> 1.1 \times 10^{-1}$	$> 940$
Rain	Aug. 2	$2.9 \times 10^{-3}$	240
Rain	Aug. 3	$9.6 \times 10^{-3}$	800
Rain	Oct. 3 (1980)	$1.5 \times 10^{-4}$	12
Dry deposition	April 24-27	$5.7 \times 10^{-4}$	48
Dry deposition	April 28-29	$8.1 \times 10^{-4}$	67
Dry deposition	July 14-Aug. 11	$8.7 \times 10^{-4}$	72
Air	April 22-28	$1.6 \times 10^{-4}$	13
Air	April 28-May 9	$6.2 \times 10^{-5}$	5
Air	July 12-25	$1.4 \times 10^{-3}$	120
Air	July 25-Aug. 10	$4.3 \times 10^{-3}$	360
Thompson Canyon††			
Snow	1978	$8.3 \times 10^{-3}$	690
Air	1978	$1.1 \times 10^{-3}$	89
Greenland*			
Snow	1980	$5.6 \times 10^{-3}$	470
Air	1980	$4.5 \times 10^{-4}$	38
Average crustal value**		$1.2 \times 10^{-5}$	

† Lead computed from washout factor and air concentration (see text).

†† Elias et al. [1982].

\* Davidson et al. [1981].

\*\* Chow and Patterson [1962].

it is most often used to identify different sources of industrial lead. The origin of aerosols emitted from land sources that are contained in the North Pacific Easterlies varies systematically with season. Both we (Table 1) and Duce et al. [1980] observed that the concentrations of silicate dusts in air at Enewetak decreased by a factor of about 50 from April to August 1979. Duce et al. [1980] assigned an Asian origin to these dusts on the basis of retrospective studies of air trajectories. Table 2 shows that the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio in aerosols collected on filters in April, when concentrations of silicate dust were highest, were similar to the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio in lead aerosols emitted from Asia and Japan (Table 5). Table 2 shows that later the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio in aerosols collected on filters, when concentrations of silicate dust had decreased about 50-fold, was more like the  $^{206}\text{Pb}/^{207}\text{Pb}$  in lead aerosols emitted from the United States (Table 5). This isotopic change substantiates the interpretations made from the air trajectory analysis that high concentrations of dust during the dry season at Enewetak originated from Asia and that later, during the wet season, aerosols emitted from land sources originated mainly from North America.

The isotopic composition of lead in seawater near Enewetak is not the same as the isotopic composition of lead measured in rain at that location. Lead in seawater is an integrated mixture of different leads accumulated over a period of several years. The isotopic composition of lead in air varies from time to time as a function not only of seasonal changes in the proportions of industrial leads from different lands, but also because the isotopic composition of industrial lead emitted from a given land source changes with time as a result of changing proportions of ores originating from different geological deposits. For example, the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio in gasoline exhaust lead in the western United States changed from about 1.145 in 1963 to about 1.225 in 1978 [Chow et al., 1975; Shirahata et al., 1980]. An example of seasonal changes in lead isotopic composition has been discussed above.

The isotopic composition of lead in surface seawater does change slowly with time and is different at different geographic locations; but such changes that do occur with time are very much slower than those occurring in the air over the seas. The residence time of lead in the atmosphere is about 10 days [Nriagu, 1978], while

TABLE 5. Estimated Average Isotopic Compositions of Industrial Lead Emissions to the Atmosphere From Major Continental Source Regions.

Source Region		$^{206}\text{Pb}/^{207}\text{Pb}$
Western Canada	(1979)	1.195
Western United States	(1974)	1.190
Western United States	(1978)	1.230
Mexico/Brazil	(1978)	1.187
Asia/Japan	(1978)	1.153 to 1.165
Australia	(1978)	1.140

From air filters, gasolines, and lead ores produced and used [Ng and Patterson 1982; Stukas and Wong, 1981; Doe 1970; Murozumi, 1981].

the residence time of lead in surface seawater is 1 to 2 years [Schaule and Patterson, 1981]. The geographic distribution of lead concentrations and isotopic compositions in surface waters of the central Pacific (Table 2) show systematic decreases in Pb concentrations from about 11 pg/g at 20°N through about 6 pg/g in equatorial waters to 4 pg/g at 18°S.  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios decrease systematically from 1.196 at 15°N to 1.182 at 4°N to 1.176 at 2° to 15°S [Flegal et al., 1981]. These gradients are consistent with a greater input from atmospheric sources of industrial lead to the North Pacific than to the South Pacific, with the major input to the North Pacific Easterlies coming from North America and the major input to the South Pacific Easterlies coming from Australia and Mexico. The  $^{206}\text{Pb}/^{207}\text{Pb}$  in air measured a few times on an event basis at Enewetak ranged from 1.170 to 1.205 (Table 2). It is more or less fortuitous that the mean should be about the same as that in surface seawater at Enewetak. The isotopic compositions of Pb in rain and dry deposition do not show such an agreeable mean, however, because they are event samples, and the sampling times were not equitable. In 1979, the mean isotopic composition of Pb in the total annual input by rain and dry deposition at Enewetak, if it could be determined, would probably be more radiogenic than that in surface seawater because, as has been mentioned earlier, the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of U.S. industrial lead has increased in recent years and the lead in surface seawater is older than its current annual input. The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio in surface waters at Enewetak shows that surface seawater lead from the 10°N section of the north-south track that has been studied across the Central Pacific has traveled westward to Enewetak. The  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in atmospheric leads from both Asia/Japan and Australia/South America are similar; and since equatorial Pacific waters appear to be homogenized through mixing across a rather broad band [Flegal et al., 1981], it is unclear whether the nonradiogenic component of lead in surface seawater at Enewetak comes from Asia/Japan or Australia/South America or both.

#### Dry Deposition and Precipitation Mechanisms

It has been shown that the bulk of the lead in air samples is associated with particles less than 0.4  $\mu\text{m}$  in diameter [Duce et al., 1982]. This is consistent with observations on land which also show that these lead-rich anthropogenic particles have small diameters [Mueller et al., 1972]. Calculated deposition velocities ( $\sim 10 \text{ cm s}^{-1}$ ) indicate that lead in the dry deposition deposits is associated with large diameter salt particles that deposit mainly by gravitational sedimentation and impact resulting from turbulent eddies.

**Acknowledgments.** We are indebted to the University of Hawaii and their staff at the Mid Pacific Marine Laboratory on Enewetak for provision of facilities and assistance in sample collection. We thank our colleagues in the SEAREX Program from Texas A&M University, University of Connecticut, University of Rhode Island, and Woods Hole Oceanographic Institution for assistance in field logistics and sample collection, P. Buat-Menard and R. Duce for discussions that enabled us to interpret our data correctly; G. Gill, University of Connecticut, and K. Bruland, U.C. Santa Cruz, for collecting the October 3, 1980, rain sample; and C. Davidson for a constructive review and advice concerning aerosol dynamics. This work was supported by NSF Grant OCE 77-14520. Contribution number 3735, Division of Geological and Planetary Sciences, California Institute of Technology.

#### References

- Arnold, M., P. Buat-Menard, and R. Chesselet, An estimate of the input of trace metals to the global atmosphere by volcanic activity, paper presented at RVEAC Symposium, IAMAP Third Scientific Assembly, Hamburg, Fed. Rep. of Germany, 1981.
- Broecker, W. S., *Chemical Oceanography*, p. 94, Harcourt, Brace, Jovanovich, New York, 1974.
- Bruland, K., A. Ng, B. K. Schaule and C. C. Patterson, Relationship between Pb and  $^{210}\text{Pb}$  in air, rain, and surface seawater in the North Atlantic, submitted to *Earth Plan. Sci. Lett.*, 1982.
- Buat-Menard, P., and M. Arnold, The heavy metal chemistry of atmospheric particulate matter emitted by Mount Etna volcano, *Geophys. Res. Lett.*, **5**, 245-248, 1978.
- Buat-Menard, P., M. Fontugne, and R. Chesselet, Recycling of particulate organic carbon between the surface of the ocean and the marine atmosphere, paper presented at the Symposium on the Role of the Oceans in Atmospheric Chemistry, IAMAP Third Scientific Assembly, Hamburg, Fed. Rep. of Germany, 1981.
- Chow, T. J., and C. C. Patterson, The occurrence and significance of lead isotopes in pelagic sediments, *Geochim. Cosmochim. Acta.*, **26**, 263-293, 1962.
- Chow, T. J., and C. C. Patterson, Concentration profiles of barium and lead in Atlantic waters off Bermuda, *Earth Plan. Sci. Lett.*, **1**, 397-400, 1966.
- Chow, T. J., J. L. Earl, and C. F. Bennett, Lead aerosols in the marine atmosphere, *Environ.*

- Sci. Technol., 3, 737-740, 1969.
- Chow, T. J., C. B. Snyder, and J. L. Earl, Isotope ratios of lead as pollutant source indicators, in *Proceedings, IAEA-SM-191/4*, pp. 95-108, International Atomic Energy Commission, Vienna, Austria, 1975.
- Davidson, C. I., L. Chu, T. C. Grimm, M. A. Nasta, and M. P. Qamoos, Wet and dry deposition of trace elements onto the Greenland ice sheet, *Atmos. Environ.*, 15, 1429-1437, 1981.
- Doe, B. R., *Lead Isotopes*, Springer-Verlag Berlin, New York, 1970.
- Dorman, C. E., and R. H. Bourke, Precipitation over the Pacific Ocean, 30° S to 60° N, *Mon. Weather Rev.*, 107, 896-910, 1979.
- Duce, R. A., SEAREX: A multi-institutional investigation of the sea/air exchange of pollutants and natural substances, in *Marine Pollutant Transfer Processes*, edited by M. Waldichuk, G. Kullenberg and M. Orren, Elsevier, New York, 1981.
- Duce, R. A., C. K. Unni, B. J. Ray, J. M. Prospero, and J. T. Merrill, Long range atmospheric transport of soil dust from Asia to the tropical North Pacific: Temporal variations, *Science*, 209, 1522-1524, 1980.
- Duce, R., C. K. Unni, B. J. Ray, R. Arimoto, P. J. Harder, and J. L. Fasching, Aerosol trace element composition, sources, and temporal variability in the marine atmosphere at Enewetak Atoll, submitted to *J. Geophys. Res.*, 1982.
- Elias, R., Y. Hirao, and C. C. Patterson, The input, output and distribution of lead and six other metals among biomass reservoirs in Thompson Canyon, Submitted to *Geochim. Cosmochim. Acta*, 1982.
- Engelmann, R. J., Scavenging prediction using ratios of concentrations in air and in precipitation, in *Precipitation Scavenging, USAEC Symp. Ser.*, Vol. 22, edited by W. G. N. Slinn, pp. 475-485, U.S. Atomic Energy Commission, Oak Ridge, 1970.
- Fasching, J. L., R. A. Courant, R. A. Duce, and S. R. Piotrowicz, A new surface microlayer sampler utilizing the bubbling microtome, *J. Rech. Atmos.*, 8, 649-652, 1974.
- Flegal, A. R., B. K. Schaule, D. M. Settle, and C. C. Patterson, Lead concentrations and stable isotopic compositions in surface waters of the Central Pacific, *Eos Trans. AGU*, 62, 894, 1981.
- Mason, B., *Principles of Geochemistry*, p. 44, John Wiley, New York, 1960.
- Mueller, P. K., T. A. Cahill, and A. E. Alcocer, Chemical composition of Pasadena aerosol by particle size and time of day, in *Aerosols and Atmospheric Chemistry*, edited by G. Hidy, p. 306, Academic, New York, 1972.
- Murozumi, M., T. J. Chow, and C. C. Patterson, Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata, *Geochim. Cosmochim. Acta*, 33, 1247-1294, 1969.
- Ng, A., and C. C. Patterson, Natural concentrations of lead in ancient Arctic and Antarctic ice, *Geochim. Cosmochim. Acta*, 45, 2109-2121, 1981.
- Ng, A., and C. C. Patterson, Changes of Pb and Ba with time in California offshore basin sediments, *Geochim. Cosmochim. Acta*, in press, 1982.
- Nozaki, Y., D. J. DeMaster, D. M. Lewis, and K. K. Turekian, Atmospheric  $^{210}\text{Pb}$  fluxes determined from soil profiles, *J. Geophys. Res.*, 83, 4047-4051, 1978.
- Nozaki, Y., J. Thomson, and K. K. Turekian, The distribution of Pb-210 and Po-210 in the surface waters of the Pacific Ocean, *Earth Planet. Sci. Lett.*, 32, 304-312, 1976.
- Nozaki, Y., K. K. Turekian, and K. Von Damm, Pb-210 in GEOSECS water profiles from the North Pacific, *Earth Planet. Sci. Lett.*, 49, 393-400, 1980.
- Nriagu, J. O., Lead in the atmosphere, in *The Biochemistry of Lead in the Environment*, Vol. 1A, edited by J. O. Nriagu, pp. 137-184, Elsevier, New York, 1978.
- Patterson, C. C., Lead in seawater workshop, *Science*, 183, 553-554, 1974.
- Patterson, C. C. in SEAREX- Sea Air Transport-Exchange of Pb, Ca, Sr, Ba, K, Rb, Cs, Rep. OCE77-14520, p. 6, Nat. Sci. Found., Washington, D.C., 1981.
- Patterson, C. C., and A. Ng, An upper limit for the enrichment of lead in seaspray compared to seawater determined in seaspray generated by a bubble interfacial microlayer sampler, submitted to *Earth Planet. Sci. Lett.*, 1982.
- Patterson, C. C., and D. M. Settle, Contribution of lead via aerosol impact to the Southern California Bight, *J. Rech. Atmos.*, 8, 957-960, 1974.
- Patterson, C. C., and D. M. Settle, The reduction of order of magnitude errors in lead analyses of biological materials and natural waters by evaluating and controlling the extent and sources of industrial lead contamination introduced during sample collecting and analysis, in *Accuracy in Trace Analysis*, Spec. Publ. 422, edited by P. La Fleur, pp. 321-351, National Bureau of Standards, Washington, D.C., 1976.
- Patterson, C., and D. Settle, SEAREX research notes, *SEAREX Newslett.*, 2, 10-13, 1979.
- Patterson, C. C., D. M. Settle, C. K. Unni, and R. A. Duce, Magnitude of lead flux to the atmosphere from volcanoes, submitted to *J. Geophys. Res.*, 1982.
- Pytkowicz, R. M., and D. R. Kester, The physical chemistry of seawater, in *Annual Review of Oceanographic Marine Biology*, Vol. 9, edited by H. Barnes, Harper and Row, New York, 1971.
- Schaule, B. K., Zur ozeanischen Geochemie des Bleis--Nachweis einer anthropogenen Störung anhand kontaminationkontrollierter Bleikonzentrationsmessungen im offenen Nord-Pazifik, Dissertation, Univ. Heidelberg, Fed. Rep. of Germany, 165 pp., 1979.
- Schaule, B., and C. C. Patterson, The occurrence of lead in the Northeast Pacific and the effects of anthropogenic inputs, in *Lead in the Marine Environment*, edited by M. Branica and Z. Konrad, pp. 31-43, Pergamon, New York, 1980.
- Schaule, B. K., and C. C. Patterson, Lead concentrations in the Northeast Pacific: evidence for global anthropogenic perturbations, *Earth Planet. Sci. Lett.*, 54, 97-116, 1981.
- Schaule, B. K., and C. C. Patterson, Perturbations of the natural lead depth profile in the Sargasso Sea by industrial lead, in *Trace Metals in Sea Water*, Plenum, New York, 1982.
- Settle, D. M., and C. C. Patterson, Lead in albacore: Guide to lead pollution in Americans, *Science*, 207, 1167-1176, 1980.
- Settle, D. M., R. A. Duce, and C. C. Patterson,

- Importance of transfer in the atmosphere of metal-rich sub-micrometer particles to large particles in determining magnitudes of dry deposition fluxes of metals to the ocean, paper presented at, ROAC Symposium, IAMAP Third Scientific Assembly, Hamburg, Fed. Rep. of Germany, 1981.
- Settle, D. M., C. C. Patterson, K. K. Turekian, and J. K. Cochran, Lead precipitation fluxes at tropical oceanic sites determined from  $^{210}\text{Pb}$  measurements, J. Geophys. Res., 87, 1239-1245, 1982.
- Shirahata, H., R. W. Elias, and C. C. Patterson, Chronological variations in concentrations and isotopic compositions of anthropogenic atmospheric lead in sediments of a remote subalpine pond, Geochim. Cosmochim. Acta, 44, 149-161, 1980.
- Stukas, V. J., and C. S. Wong, Stable lead isotopes as a tracer in coastal waters, Science, 211, 1424-1427, 1981.
- Tatsumoto, M., and C. C. Patterson, The concentration of common lead in seawater, in Earth Science and Meteoritics, edited by J. Geiss and E. D. Goldberg, pp. 74-89, North Holland Publishing Co., Amsterdam, 1963a.
- Tatsumoto, M., and C. C. Patterson, Concentrations of common lead in some Atlantic and Mediterranean waters and in snow, Nature, 199, 350-352, 1963b.
- Trefry, J. H., and B. J. Presley, Heavy metal transport from the Mississippi River to the Gulf of Mexico, in Marine Pollutant Transfer, edited by H. Windom and R. Duce, pp. 39-76, D. C. Heath, New York, 1976.
- Tucker, G. G., Precipitation over the North Atlantic Ocean, Q. J. R. Meteorol. Soc., 87, 147-158, 1961.
- Turekian, K. K., and J. K. Cochran,  $^{210}\text{Pb}$  in surface air at Enewetak and the Asian dust flux to the Pacific, Nature, 292, 522-524, 1981.
- Turekian, K. K., L. K. Benninger, and E. P. Dion,  $^7\text{Be}$  and  $^{210}\text{Pb}$  total deposition fluxes at New Haven, Connecticut and at Bermuda, Earth Planet. Sci. Lett., in press, 1982.
- Turekian, K. K., Y. Nozaki, and L. K. Benninger, Geochemistry of atmospheric radon and radon products, Ann. Rev. Earth Planet. Sci. 5, 227-255, 1977.

(Received January 8, 1982;  
revised June 3, 1982;  
accepted June 7, 1982.)